Enzymatic Baeyer-Villiger Oxidation of Benzo-Fused Ketones

Rioz-Martinez, Ana; de Gonzalo, Gonzalo; Pazmino, Daniel E. Torres; Fraaije, Marco W.; Gotor, Vicente

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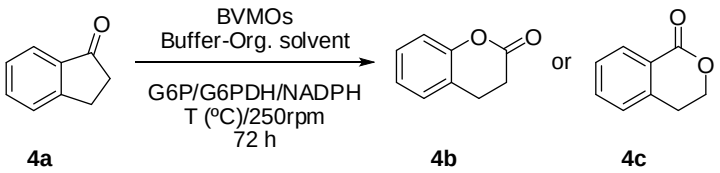
SUPPORTING INFORMATION

Title: Enzymatic Baeyer–Villiger Oxidation of Benzo-Fused Ketones: Formation of Regiocomplementary Lactones
Author(s): Ana Rioz-Martínez, Gonzalo de Gonzalo, Daniel E. Torres Pazmiño, Marco W. Fraaije, Vicente Gotor*
Ref. No.: O200900084

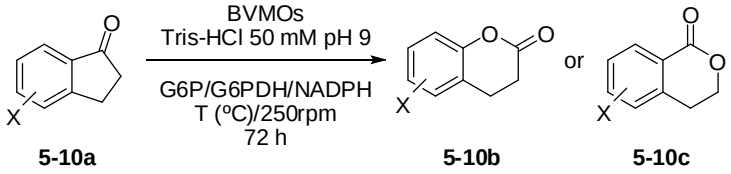
1. HAPMO and M-PAMO catalyzed oxidation of 1-indanone 4a in different buffer-organic cosolvent (5% v v^{-1}) media



Entry	BVMO	Cosolvent	log P	T (ºC)	[%] **4b**[a]	[%] **4c**[a]
1	HAPMO	None	--	20	25	≤3
2	HAPMO	MeOH	-0.76	20	11	≤3
3	HAPMO	1,4-dioxane	-0.27	20	≤3	≤3
4	HAPMO	*i*-PrOH	0.07	20	16	≤3
5	HAPMO	CH_2Cl_2	1.25	20	21	≤3
6	HAPMO	*t*BuOMe	1.35	20	25	≤3
7	HAPMO	*i*Pr_2O	2.00	20	35	≤3
8	HAPMO	toluene	2.50	20	34	≤3
9	HAPMO	2-octanol	2.72	20	39	≤3
10	HAPMO	hexane	3.50	20	44	≤3
11	M-PAMO	None	--	30	≤3	67
12	M-PAMO	MeOH	-0.76	30	≤3	79
13	M-PAMO	1,4-dioxane	-0.27	30	≤3	71
14	M-PAMO	*i*-PrOH	0.07	30	≤3	75
15	M-PAMO	CH_2Cl_2	1.25	30	≤3	12
16	M-PAMO	*t*BuOMe	1.35	30	≤3	77
17	M-PAMO	*i*Pr_2O	2.00	30	≤3	82
18	M-PAMO	toluene	2.50	30	≤3	22
19	M-PAMO	2-octanol	2.72	30	≤3	47
20	M-PAMO	hexane	3.50	30	≤3	31

[a] Determined by GC.

2. Results obtained in the BVMO-oxidation of 1-indanone derivatives 5-10a using only buffer Tris-HCl 50 mM pH 9.



5-10a **5-10b** **5-10c**

Entry	Ketone	X	BVMO	T (ºC)	[%] **5-10b**[a]	[%] **5-10c**[a]
1	**5a**	5-Cl	HAPMO	20	39	≤3
2	**5a**	5-Cl	PAMO	30	≤3	≤3
3	**5a**	5-Cl	M-PAMO	30	≤3	54
4	**6a**	6-Cl	HAPMO	20	52	≤3
5	**6a**	6-Cl	PAMO	30	≤3	4
6	**6a**	6-Cl	M-PAMO	30	≤3	52
7	**7a**	5-Br	HAPMO	20	6	≤3
8	**7a**	5-Br	PAMO	30	≤3	5
9	**7a**	5-Br	M-PAMO	30	≤3	57
10	**8a**	4-OMe	HAPMO	20	≤3	≤3
11	**8a**	4-OMe	PAMO	30	≤3	≤3
12	**8a**	4-OMe	M-PAMO	30	≤3	35
13	**9a**	5-OMe	HAPMO	20	13	≤3
14	**9a**	5-OMe	PAMO	30	≤3	≤3
15	**9a**	5-OMe	M-PAMO	30	≤3	26
16	**10a**	6-OMe	HAPMO	20	32	≤3
17	**10a**	6-OMe	PAMO	30	≤3	≤3
18	**10a**	6-OMe	M-PAMO	30	≤3	≤3

[a] Determined by GC.

3. GC analyses

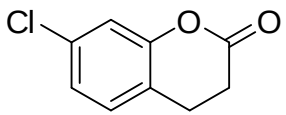
The following columns were used for the determination of conversions: A: Restek RT-BetaDEXse (30 m x 0.25 mm x 0.25 µm, 12 psi N_2) and B: Hewlett Packard HP-1 (30m x 0.32 mm x 0.25µm, 12.2 psi N_2).

Table 1. Determination of conversion values by GC.

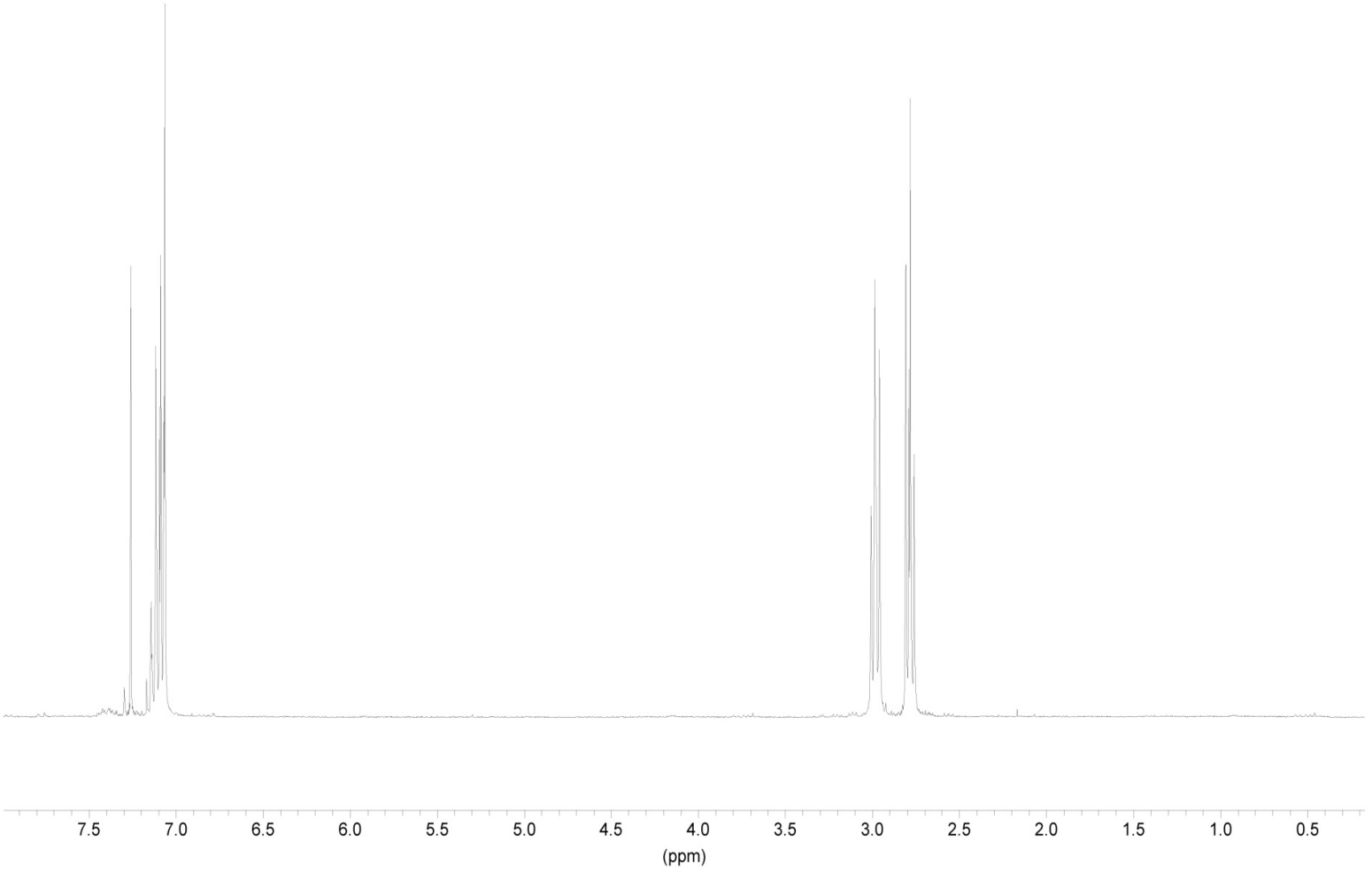
Substrate	Program[a]	Column	t_R [min] **1-11a**	t_R [min] **1-11b**	t_R [min] **4-10c**
1	70/5/3/180	A	37.1	42.2	--
3	70/5/3/180	A	32.0	45.5	--
4	70/5/3/180	A	33.5	40.1	44.1
5	70/5/3/200/5	A	41.9	48.8	51.8
6	70/5/3/200/5	A	41.5	48.0	51.9
7	100/5/2/160	B	12.7	17.4	23.9
8	100/5/3/200/5	A	34.4	39.3	44.5
9	100/5/3/200/15	A	36.1	41.0	50.1
10	100/5/3/200/10	A	33.5	39.8	42.8
11	70/5/3/180	A	22.3	29.6	--

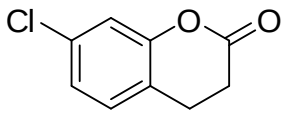
[a] Program: initial T (ºC)/ time (min)/ slope (ºC/min)/T (ºC)/ time (min)/

4. NMR Spectra

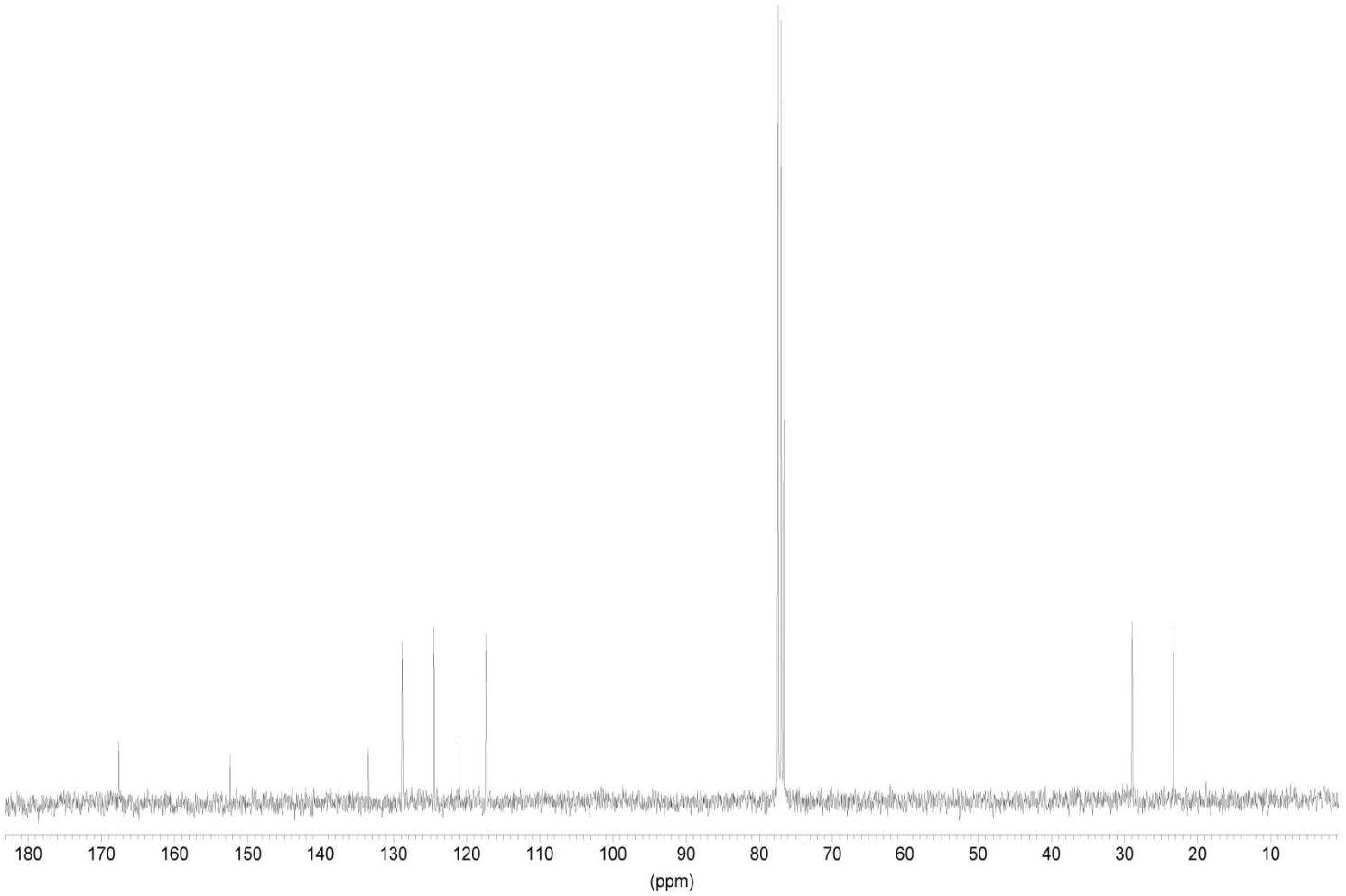


(±)-**6b**




Cl
O
O

(±)-**6b**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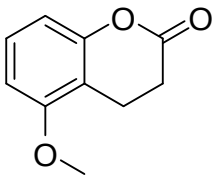
10
(ppm)



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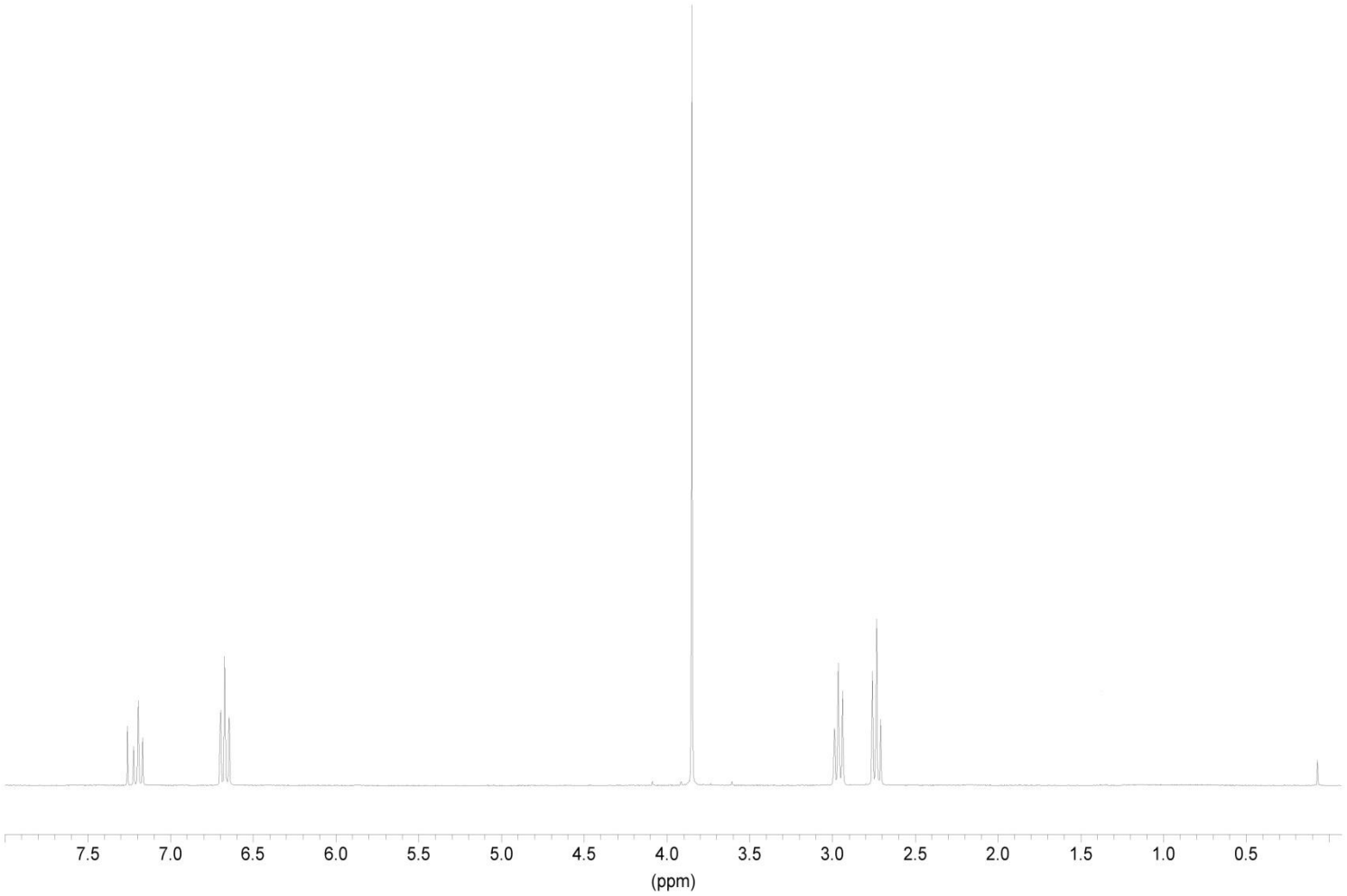

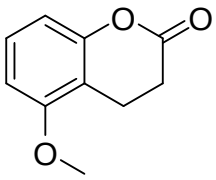

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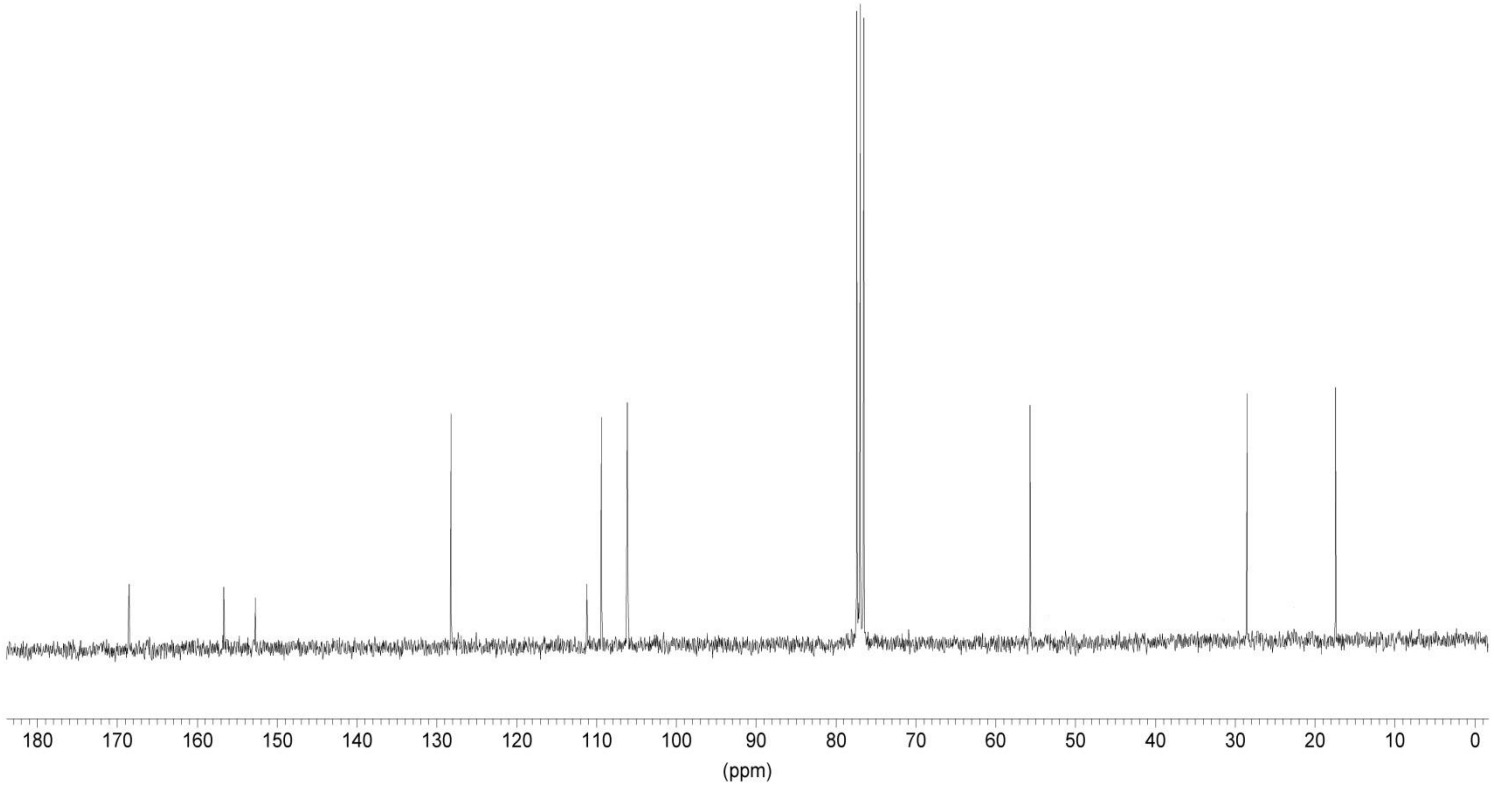
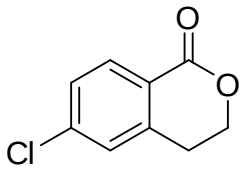
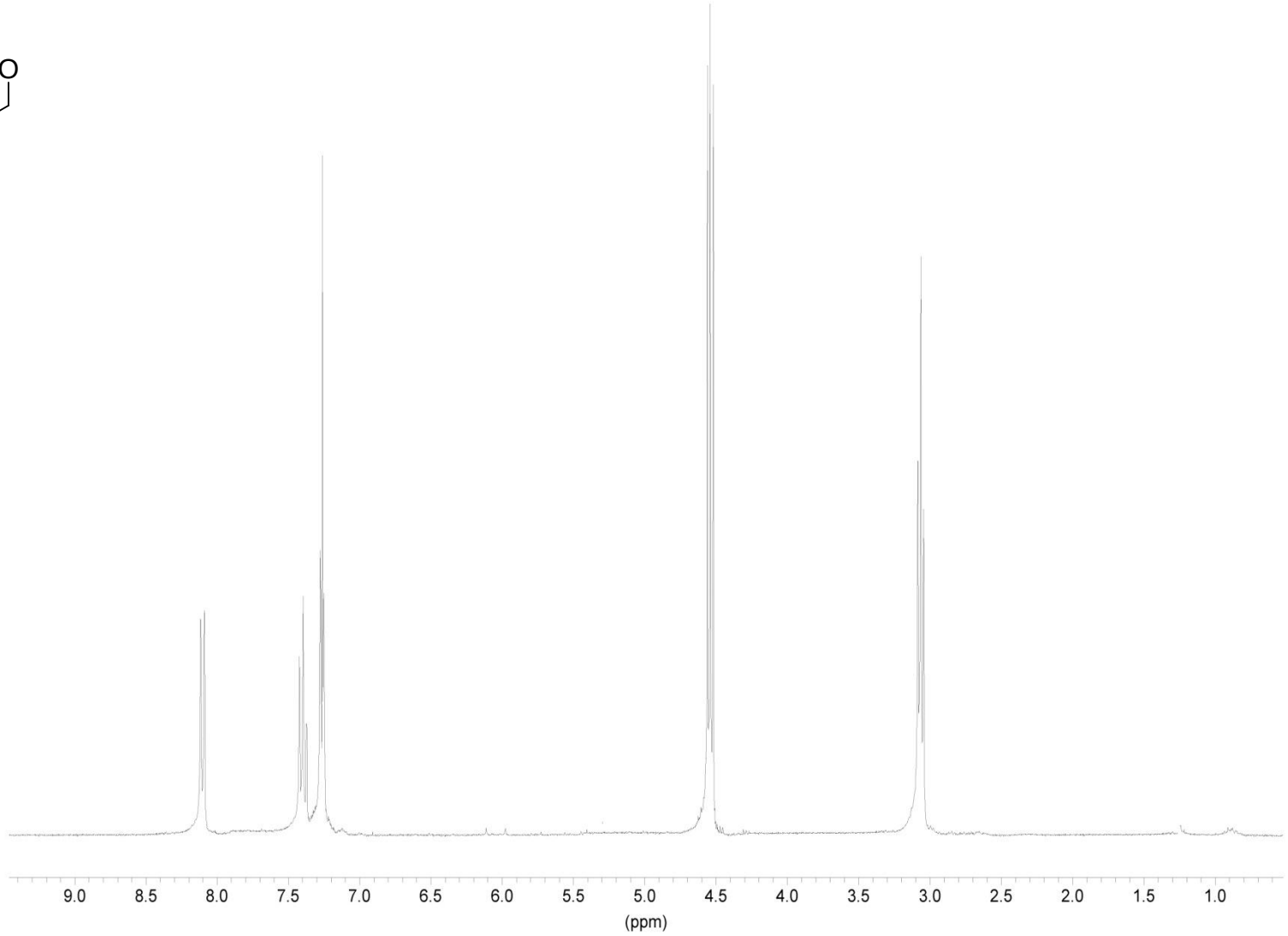
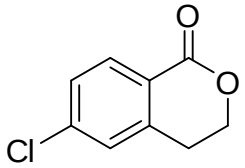


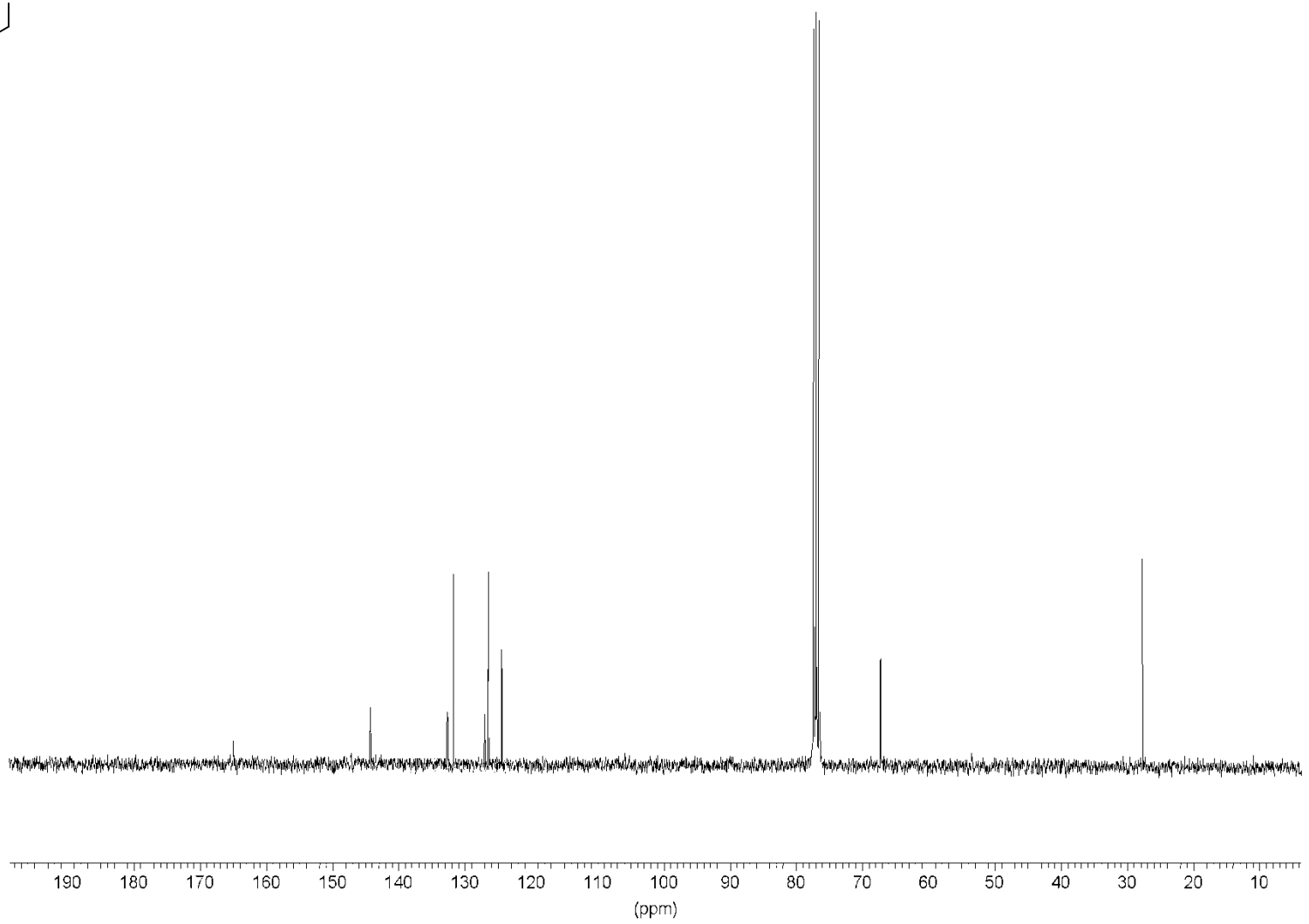


(±)-**5c**




O
O
Cl

(±)-**5c**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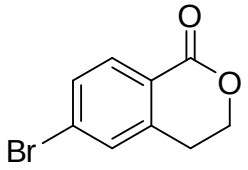
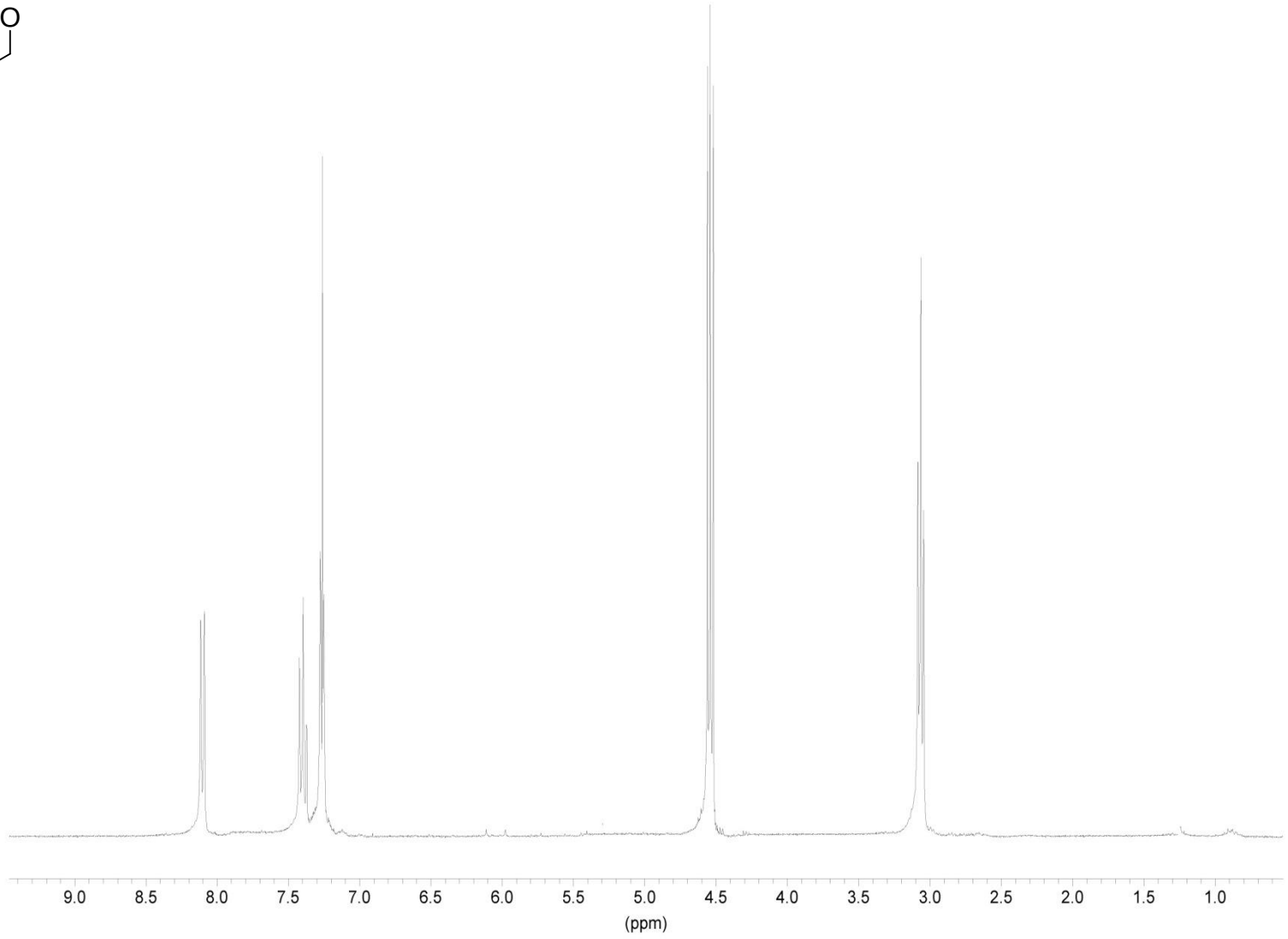
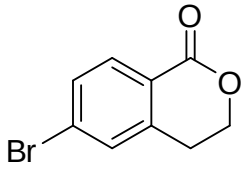
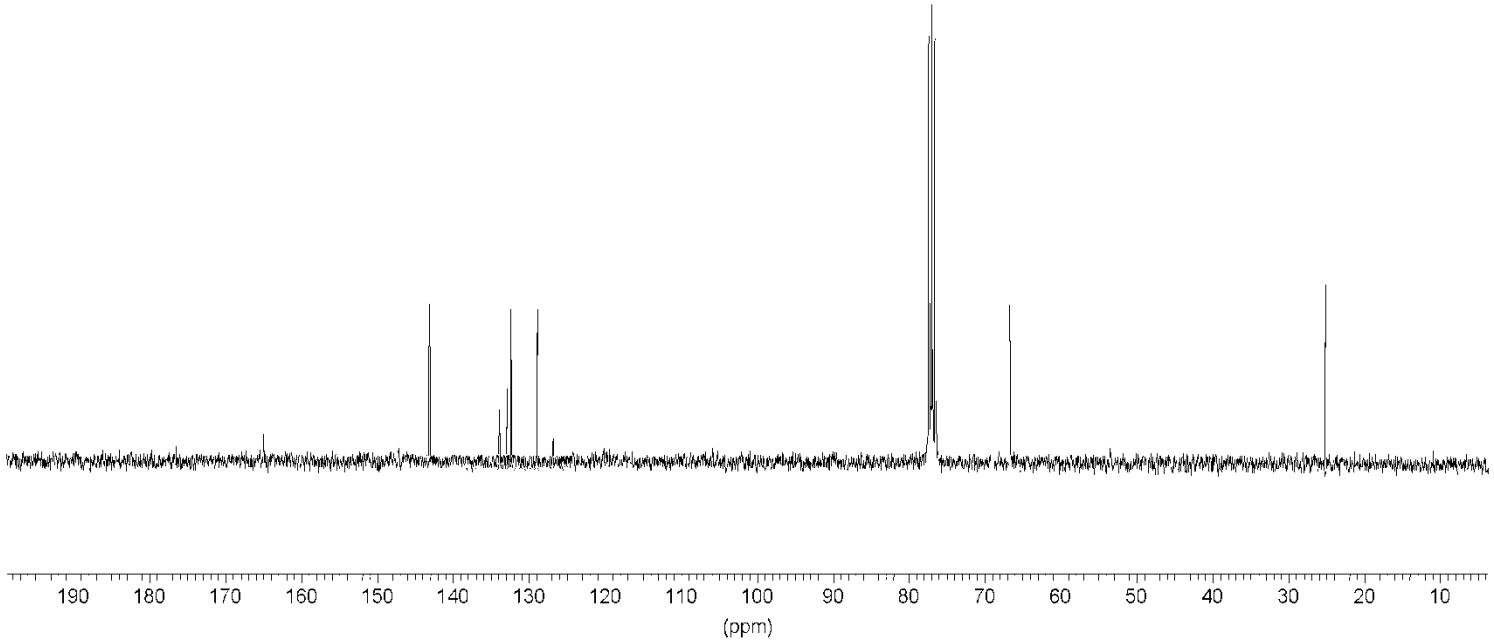


(±)-**7c**




O
O
Br

(±)-**7c**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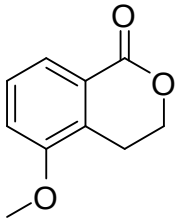
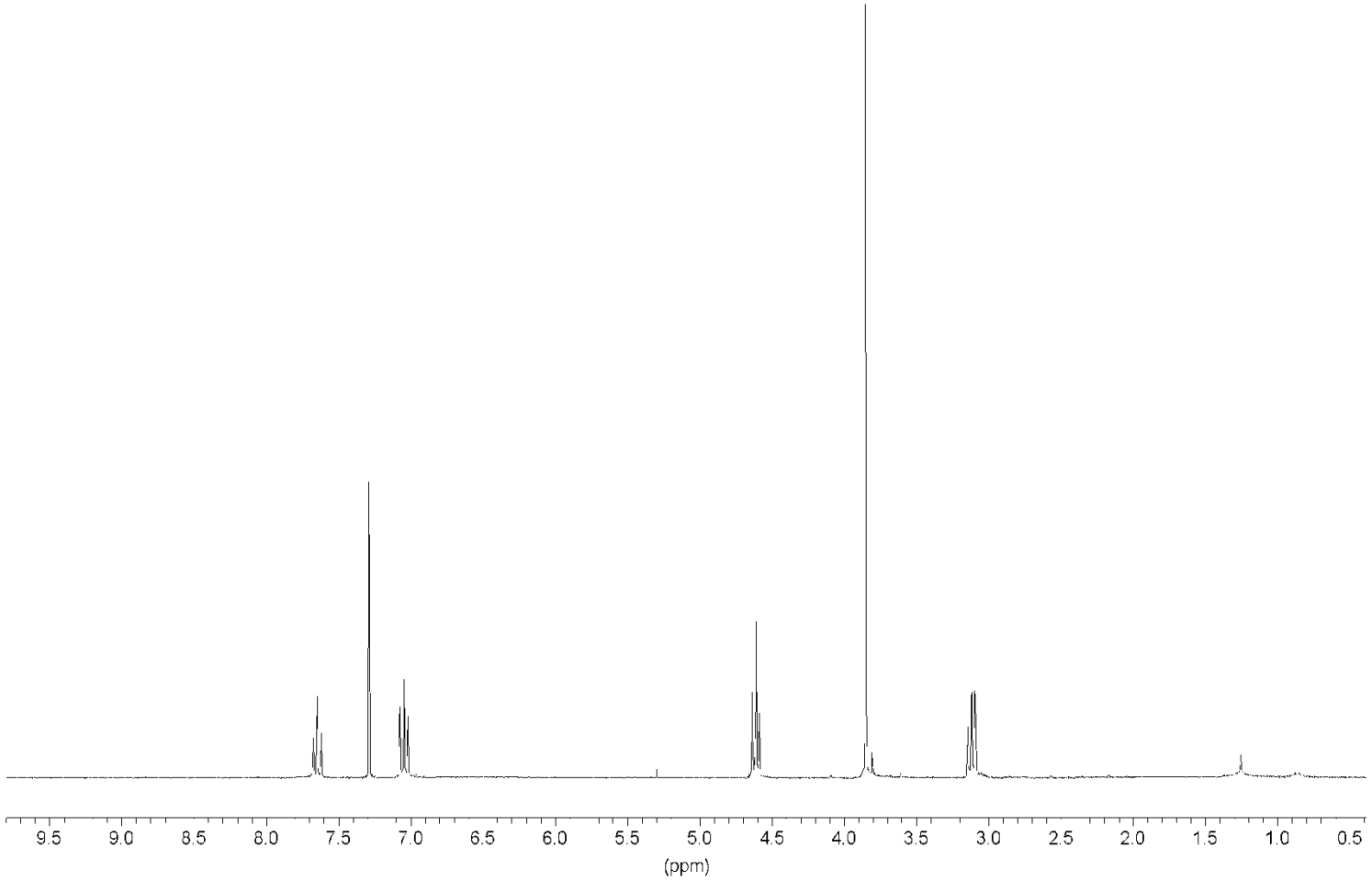
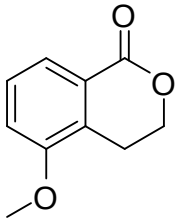
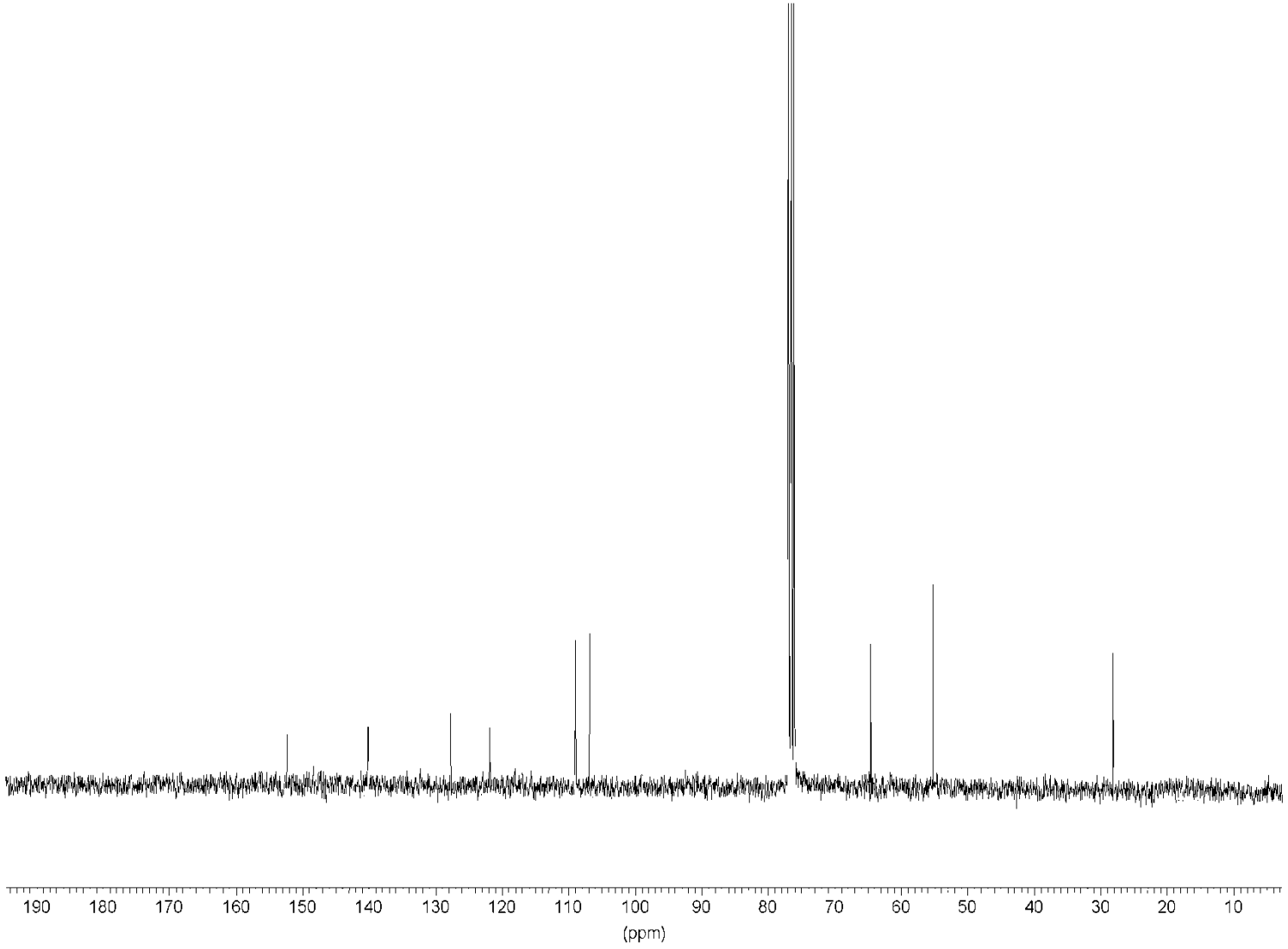


(±)-**8c**




O
O
O

(±)-**8c**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